Synthesis of magnetic mesoporous metal-organic framework-5 for the effective enrichment of malachite green and crystal violet in fish samples

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ABSTRACT

A novel, magnetic and mesoporous Fe_3O_4@PEI-MOF-5 material was synthesized for the effective enrichment of malachite green (MG) and crystal violet (CV) in fish samples. The Fe_3O_4@PEI-MOF-5 material was prepared by a facile two-step solvothermal approach in which Fe_3O_4@PEI and MOF-5 were connected through chemical bonds. Characterization of the newly synthesized Fe_3O_4@PEI-MOF-5 material was performed by Fourier transform infrared spectroscopy, X-ray diffractometry, vibrating sample magnetometry, scanning electron microscopy, transmission electron microscopy, thermogravimetric analysis and X-ray photoelectron spectroscopy. This new material was determined to have high magnetization and chemical stability, a large surface area and a distinctive morphology. An effective enrichment and detection method for MG and CV was subsequently developed by combining the Fe_3O_4@PEI-MOF-5 material with ultra-high-performance liquid chromatography–tandem mass spectrometry. The linearity ranges of this approach for MG and CV were 1–500 ng/mL and 0.25–500 ng/mL, respectively, with correlation coefficients (R^2) of 0.999. The limits of detection (LODs) of the method for MG and CV were 0.30 ng/mL and 0.08 ng/mL, respectively, indicating that the Fe_3O_4@PEI-MOF-5 material had good adsorption properties for MG and CV. Fe_3O_4@PEI-MOF-5 can be expected to also provide efficient enrichment of MG and CV in other complex matrices.

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1. Introduction

Malachite green (MG) and crystal violet (CV), members of the class of triphenylmethane dyes, have played an important role in the sterilization and disinfection processes of aquaculture operations [1,2]. Due to their low cost and high efficiency [3–5], MG and CV are widely used to control external fungi and parasites in aquarium fish and fish eggs [6–9]. However, in recent years, the illegal use of MG and CV has attracted considerable attention because of the potential harm that these dyes can cause to humans. For example, MG and CV can affect the human immune and reproductive systems and thus threaten human health [10]. In consideration of food safety and public health, many countries have banned the use of MG and CV in aquaculture operations [11,12]. Therefore, development and validation of a highly sensitive and accurate analytical method for the detection of MG and CV in complex matrices are of vital importance [13].

Sample pretreatment is the most important step in sample analysis, especially for complex sample matrices [14,15]. Many methods have been applied to eliminate the influence of the matrix, including solid-phase extraction (SPE) [16], solid-phase microextraction (SPME) [17], liquid–liquid extraction (LLE) [18], liquid-phase microextraction (LPME) [19] and magnetic solid-phase extraction (MSPE) [20]. MSPE is a new type of magnetically modified or magnetic SPE. Compared with SPE, the magnetic nanoparticles of MSPE have a larger specific surface area and shorter diffusion distance for the analytes, which enables the rapid separation of the magnetic materials and solutions through application of a magnetic field, thereby further reducing the sample processing time [21–23]. Magnetic materials have been rapidly developed in recent years, and magnetic separation has been widely used in a variety of areas as a result [24–26]. The magnetic particles applied in MSPE usually consist of magnetic

iron oxides and iron minerals such as Fe_3O_4 [27], which is the most commonly used magnetic material with high magnetization [28]. Fe_3O_4 nanoparticles have also been modified with different sorbents, such as phytic acid-stabilized graphene oxide (GOPA) [29], polypyrrole-polyaniline (PPy-PANI) [30], and graphene oxide (GO) [31]. However, most of the sorbents are small molecules that are typically bound to the Fe_3O_4 particles through unstable non-covalent interactions. Metal-organic frameworks (MOFs) are composed of inorganic metals and bridging organic ligands, which interconnect through self-assembly to form a crystalline porous material with a periodic network structure [32]. MOFs have recently been applied in compound separation [33,34] and drug delivery [35,36]. MOF-5, a type of MOF, was first reported in 1999 [37] and has several advantageous characteristics, such as a high specific surface area, large pore volume, and multiple functional groups on the surface [38]. A large number of aromatic rings are present in MOF-5, which allows it to strongly adsorb compounds with π-π structures, such as MG and CV.

In this study, a novel, magnetic and mesoporous material, Fe_3O_4@PEI-MOF-5, was synthesized for the first time through a two-step solvothermal method. Characterization of the new Fe_3O_4@PEI-MOF-5 material indicated that it possesses high magnetization, a large surface area and a distinctive morphology. The newly synthesized material also exhibited excellent adsorption capabilities for the MG and CV targets. An effective enrichment and detection method for MG and CV was subsequently developed by combining ultra-high-performance liquid chromatography-tandem mass spectrometry (UHPLC–MS/MS) with Fe_3O_4@PEI-MOF-5. This new method was then successfully validated and applied to the analysis of MG and CV in fish samples.

2. Experimental

2.1. Chemicals and materials

CV (96%), MG (96%), zinc acetate dihydrate ($Zn(OAc)_2 \cdot 2H_2O$, 99%), terephthalic acid (H_2BDC, 99%), formic acid (98%) and acetic acid (99.8%) were purchased from J&K (Beijing, China). Ethylene glycol, N,N-dimethylformamide (DMF) and ethanol (EtOH) were all of analytical grade and purchased from Sinopharm Chemical Reagent Co, Ltd. (Dalian, China). Iron(III) chloride hexahydrate ($FeCl_3 \cdot 6H_2O$, $\geq$98%), sodium acetate (CH_3COONa, $\geq$99%) and dichloromethane (CH_2Cl_2, $\geq$99.8%) were obtained from Sigma-Aldrich (Shanghai, China). Methanol (99.9%) and acetonitrile (99.9%) were purchased from Merck (Dalian, China). Polyethyleneimine (PEI, branched, MW 600, 99%) was purchased from Alfa (Beijing, China). Standard solutions were diluted with EtOH and stored at 4 °C.

2.2. Instrumental analysis

Changes in the surface groups of MOF-5 and Fe_3O_4@PEI-MOF-5 were observed with a Fourier transform infrared (FT-IR) spectrometer (Nicolet iS50, Thermo Fisher Scientific, USA). X-ray photoelectron spectroscopy (XPS) (ESCALAB 250Xi, Thermo Scientific) was used to analyse the functional groups of the magnetic and mesoporous MOF. X-ray diffractometry (XRD) (X'pert Pro-1, PAN-Alytical, Holland) was used to determine the internal structure of the material. The surface morphology was observed by scanning electron microscopy (SEM) (JSM-7800F, JEOL, Japan). Transmission electron microscopy (TEM) (JEM-200EX, JEOL, Japan) was used to characterize the size and shape of the material. A vibrating sample magnetometer (VSM) (JDM-13, Jilin University, China) was used to obtain the magnetization curve of Fe_3O_4@PEI-MOF-5. The stability

of the magnetic Fe_3O_4@PEI-MOF-5 material was evaluated with a thermogravimetric (TG) analyser (STA 449 F3, Netzsch, Germany).

MG and CV were separated by using an Agilent 1290 UHPLC system and a C18 column (50 mm length $\times$ 2.1 mm i.d., 1.7 μm, Waters, USA) and detected by using an Agilent QQQ mass spectrometer (6460) with an electrospray ionization (ESI) ion source in multiple reaction monitoring (MRM) mode. The column temperature was maintained at 30 °C. The mobile phase was 0.2% formic acid in water (A) and acetonitrile (B). The UHPLC elution gradient started with 25% phase B and increased to 95% B at 4 min, which was maintained for 3 min. Finally, the elution gradient decreased to 25% B at 9 min, which was maintained for 2 min to equilibrate the column. The flow-rate of the mobile phase was 0.2 mL/min, and the injection volume was 1 μL.

2.3. Synthesis of the magnetic Fe_3O_4@PEI-MOF-5 material

The magnetic Fe_3O_4@PEI-MOF-5 material was synthesized through a two-step solvothermal method. First, the Fe_3O_4@PEI magnetic nanoparticles were synthesized according to a previously reported method [39]. In brief, 2.0 g of $FeCl_3 \cdot 6H_2O$ was dissolved in 100 mL of ethylene glycol by sonication to generate a yellow solution. Then, 8.0 g of CH_3COONa and 2.0 g of PEI were added to the yellow solution. After stirring at 60 °C for 20 min, the mixture was transferred to a 200 mL Teflon-lined autoclave and maintained at 220 °C for 2 h. After cooling to room temperature, the sediments were collected, washed with EtOH and DMF three times each, and dispersed in DMF. Next, the obtained MOF-5 was modified with Fe_3O_4@PEI magnetic nanoparticles according to the previous report [40]. Typically, 0.4910 g of H_2BDC and 1.688 g of $Zn(OAc)_2 \cdot 2H_2O$ were dispersed in 20 mL and 25 mL of DMF, respectively, and dissolved by sonication. The $Zn(OAc)_2 \cdot 2H_2O$ solution was then added to the H_2BDC solution, and the mixture was stirred at room temperature. Then, Fe_3O_4@PEI dispersed in DMF was added to the mixed solution under sonication, which was continued for 30 min. After complete dispersion, the mixture was transferred to a 200 mL Teflon-lined autoclave and maintained at 120 °C for 10 h. The sediments were washed with DMF and CH_2Cl_2 three times each and then dispersed in CH_2Cl_2 for 15 h at room temperature. The obtained products were dried at 120 °C for 12 h under vacuum.

2.4. Sample preparation

Fish samples were obtained from a local market (Dalian, China). First, the bones and skin were removed, and then the fish were homogenized. All fish samples were stored at −80 °C. Before extraction, the fish samples were thawed at room temperature. A 2.0 g portion of the fish sample and 10 mL of acetonitrile were transferred to a 50 mL centrifuge tube, which was sonicated for 10 min. The 50 mL centrifuge tube was then centrifuged at 15,000 rpm for 1 min, and the extract was collected in a second 50 mL centrifuge tube. The fish samples were extracted three times using the same method. Finally, the extract was dried with nitrogen and stored at 4 °C.

2.5. Analysis of fish samples by Fe_3O_4@PEI-MOF-5

The dried extract was dissolved in 1 mL of EtOH, and a suitable amount of the magnetic Fe_3O_4@PEI-MOF-5 material was added to the solution. The mixture was shaken for 40 min and separated with a magnet. Then, the supernatant was removed, and the material was washed 3 times with 1 mL of ethanol. Finally, the analytes were eluted in methanol containing 1% formic acid, and the desorption time was 20 min. UHPLC–MS/MS was applied to analyse above elute solution.